The Determination of the Osmotic Pressures of Solutions by the Measurement of their Vapour Pressures.

By the Earl of Berkeley and E. G. J. Hartley, B.A. (Oxon.).

In May, 1903, we described,[*] in a preliminary paper, some experiments by which we had measured directly the osmotic pressures of strong solutions of cane sugar in water. Since then a repetition of the experiments with an improved apparatus has been carried out, the results of which we hope to publish very shortly.

As these results depart widely from the theoretical gas laws, it was deemed advisable to obtain the osmotic pressures of the same solutions by an independent method; and an experimental investigation of the well known connection between the "lowering" of the vapour pressure of a solution and its osmotic pressure seemed suitable.

After some experiments with a dew point method, the dynamical method due to Ostwald and Walker was selected, as it promised to be a rapid one and to be capable of giving results both with the solutions, the osmotic pressures of which we had already measured, and those where the osmotic pressures are higher than direct measurements can reach; also it is applicable to solutions of substances for which no semipermeable membranes have yet been found.

The method is described by Ostwald[†] as follows: "Two Liebig's potash bulbs containing the solution, and one containing the water, are connected with each other. The last is weighed, and is in its turn connected with a U-tube containing pumice soaked in sulphuric acid. A current of air is drawn through the apparatus. The air first saturates itself up to the vapour pressure of the solution then takes up from the water the quantity of vapour necessary for complete saturation, all of which it finally gives up to the sulphuric acid. The loss of weight of the water vessel is to the increase of weight of the sulphuric acid as the difference between the vapour pressure of the solution and of pure water is to the vapour pressure of pure water."

It was thought advisable to modify the general arrangement so as to obtain a closer knowledge of the best conditions for carrying out an experiment. With this in view, the air, before entering the solution, was completely dried by

[*] 'Roy. Soc. Proc.,' vol. 73, p. 436.

[†] Ostwald, 'Physical Chem. Measurements,' p. 188, Walker's translation, 1894.

passing through sulphuric acid, but the remainder of the train of vessels corresponded to the arrangement described above. Then by weighing the two vessels containing the solution, three objects were attained: (1) The weight lost by the solution is a direct measure of its vapour pressure, and consequently this loss in conjunction with the loss of weight of the water vessel gives a value for the ratio of the two vapour pressures to one another; (2) it is evident that the sum of the losses in weight of the solution and water vessels should equal the gain in weight in the vessel containing the sulphuric acid. This, it was hoped, would give a test as to the value of the particular experiment. It was found, however, that a small quantity of water always condensed in the junction leading from the water vessel to the sulphuric acid, and was therefore lost;* hence the gain in weight of the sulphuric acid was not used in the calculations; (3) by weighing the second vessel containing the solution an insight is afforded into the question as to whether the air, on emerging from the first vessel, was saturated up to the vapour pressure of the solution or not. We would draw attention to this, as it seems an important guide to the weight to be attributed to the experiment.

Testing the Efficacy of the Method.—This second vessel always lost weight, and numerous experiments were carried out in the endeavour to find the cause. The loss occurred in spite of alterations in the rate of bubbling, or in the forms of the absorption tubes. Eventually the explanation was found in the following fact.†

If air be passed through two absorption bulbs, which are filled with water, and connected together, the bubbles, owing to the difference in hydrostatic pressure, will increase in volume during their passage. Consequently, the air, although saturated on leaving the first bulb, will take up yet more water vapour from the second.

Another error which may occur with the bubbling method, is that particles of fine spray may be given off and thus cause loss of weight. That this occurs was shown by rapidly bubbling air in one case through sulphuric acid into a barium chloride solution, and in the other through a barium chloride solution into one of silver nitrate; in both cases there was a precipitate.

Modification of the Method.—The bubbling method was therefore discarded, and it was sought to avoid these sources of error by passing the air *over* the liquids instead of through them. Flat glass spirals were made out of $\frac{3}{4}$-inch tubing. Each spiral was about 30 inches long, and to increase the surface, they were nearly filled with glass beads.

* We hope to overcome this difficulty in the course of further experiments.
† See 'Nature,' July, 1905.

The loss of weight of the spiral containing the second solution was now considerably less than before, and with two spirals containing water there was no loss in the second. These spirals were discarded, however, owing to the unaccountable breakages which occurred, and also because it was thought that the loss in the second spiral might be due to the surface of the solution in the first spiral having become concentrated through loss of water, such loss not being compensated for by the stirring which necessarily occurs in the bubbling method.

Final Form of Apparatus.—The vessel which seems to satisfy all the requirements is shown in figs. 1, 2, and 3; the first figure is a plan, the second and third are side and end elevations respectively.

FIG. 1.   FIG. 2.   FIG. 3.
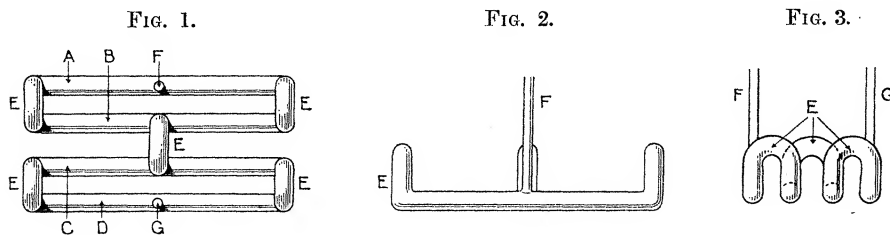
A, B, C, and D are glass tubes of about 1·5 cm. diameter and 20 cm. long; these are joined together, in the manner shown in the plan at E, by inverted **U**-tubes about 5 cm. high. F and G are the inlet and exit tubes; they are about 8 cm. long and are 0·75 cm. in diameter. The vessel is filled to about a third of its capacity with the liquid, and it will easily be seen that on slightly raising one end or the other, a clear passage for the air is obtained in that end. Thus by supporting the vessel on a platform, and oscillating the latter about an axis parallel to the line joining F G, the liquid in each of the four branches is caused to flow from one end to the other. This flow keeps the solution stirred, and also periodically wets the ends of the branches, and at the same time the contents of the branches are prevented from mixing by the air entrapped in the turned up ends.

It was considered that the fact last mentioned is of some importance, for if the rate of passage of the air be slow enough, it will practically be saturated up to the vapour pressure of the solution when it has passed through the first three branches. The solution in the fourth branch then remains at the same concentration throughout the experiment, and the air on emerging from this branch is saturated up to the vapour pressure of the original solution.

As a further help to the attainment of complete saturation, the surface

of liquid in contact with the air was increased by filling the last branch of each vessel with platinum foil rolled up into small tubes about $1\frac{1}{4}$ cm. long and $\frac{1}{4}$ cm. in diameter.

To test this apparatus, air was drawn through two of the vessels containing sodium chloride solution (75 grammes in 250 c.c.), which were joined together and placed on the oscillating platform in a water bath; two experiments were made, and in neither was the change in weight of the second vessel greater than 0·0003 gramme; the rate of passage of the air was slightly faster than that used in a determination of the lowering of the vapour pressure, and it was passed through for three days.

The Joints.—Considerable difficulty was experienced in finding a satisfactory method of joining two vessels to one another; it may, therefore, be of use to mention some of the forms of joint which failed.

By reason of the long length of time an experiment lasted, it was essential that all the vessels of the train should be as nearly as possible at the same temperature. They were, therefore, placed in a water bath; consequently the joints had to withstand the pressure due to the height of water above them, besides being impermeable to water vapour. Mr. Shaw* has shown that rubber is slightly permeable to water vapour, so plain rubber tubing was not suitable.
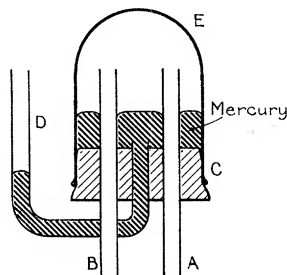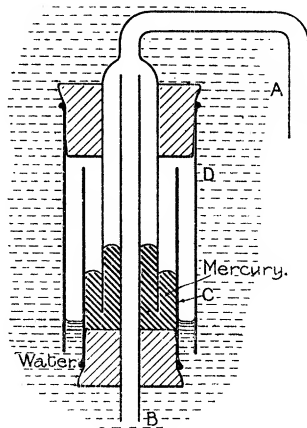
FIG. 4.

FIG. 5.

A joint shown in fig. 4 was tried. It consisted of an indiarubber plug, C, which served to support a glass dome, E, and which was perforated with three holes; two of these served for the passage of the tubes, A, B, leading to the two vessels to be joined to one another, and the third gave passage

* ‘Phil. Trans.,’ vol. 179, p. 97.

to a U-tube, D, through which mercury could be introduced so as to cover the top of the plug. This form of joint was given up owing to the difficulty of manipulation.

Another joint tried is shown in fig. 5. The tubes to be joined are A and B. A turns over as shown and widens out so as to overlap the end of B. By means of an indiarubber plug, a mercury cup, C, is supported on B, and enough mercury to close the bottom of A is placed in the cup; another tube, D, is secured to A by a plug at such a height that it overlaps the whole joint, and thus serves to keep the water of the bath off the mercury. This joint was discarded, because it was found that the alternate compression and expansion of the air inside D, due to the oscillation of the platform, caused water to be deposited on the mercury, and it was feared that some of this moisture might creep round the bottom of A.
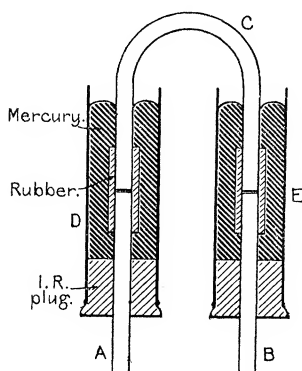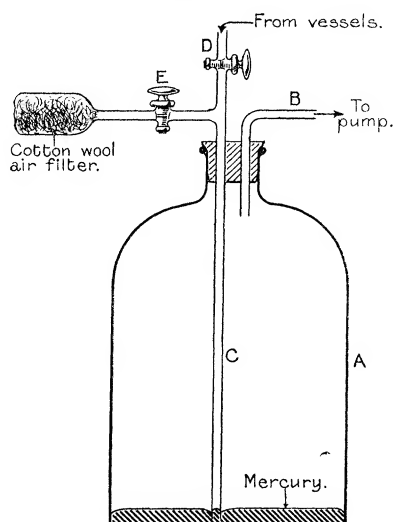
FIG. 6.

FIG. 7.

The joint which seemed the most satisfactory is shown in fig. 6. The two tubes to be joined are A and B. C is an inverted U-tube whose ends butt up against A and B, and are secured there by rubber tubing. Both joints are made tight by slipping the glass sleeves, D and E, which are carried by rubber plugs, up to a height such that the mercury in them will cover the rubber tubing to a depth of about 1 cm.

The Bath.—A large copper bath $21'' \times 14'' \times 18''$ deep was used; it was filled with water, whose temperature was kept constant by means of a thermostat. The temperature in the later experiments did not vary by more than 3/100 of a degree during the whole run of an experiment. The bath

water was kept vigorously stirred night and day by a large stirrer actuated by the laboratory shafting.

The Air Current.—The air was drawn through the train of vessels by a double acting Fleuss pump, which was driven by the laboratory shafting. To obtain as steady a stream of air as possible, the pump was connected to a large air reservoir as shown in fig. 7. A is a 10-litre glass bottle which is connected to the pump by the tube B. The tube C, which connects to the vessels through the tap D, dips under a shallow layer of mercury at the bottom of A, thus forming a kind of non-return valve. The tap E gives connection to the atmosphere, and the air current is regulated by adjusting the two taps.

The Oscillating System.—The laboratory shafting also drove a worm and wheel, and the latter, by means of a pulley cord, caused the 9-inch wheel A (see fig. 8) to revolve once in six minutes.

The platform, D E, on which the vessels stand, is rigidly connected to the arm BC, and is pivoted about C (supports not shown). A pin, F, revolving with A, and working up and down the slot, B G, communicates the requisite motion to the arm. The dimensions of the various parts are such as to cause B to travel through an arc of 20 degrees.

Fig. 8.
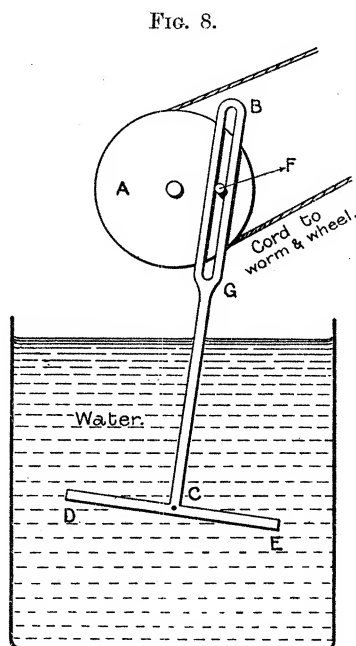
The Operation of Determining the "Lowering" of Vapour Pressure.—Fig. 9 is a diagram representing the assembled apparatus. The air enters at A, where it is filtered through cotton-wool, it then passes into the tube, B, which is nearly filled with beads moistened with sulphuric acid. On emerging from B it is led by rubber tubing into the glass spiral, C, where it takes up the temperature of the bath, and then into the sulphuric acid vessel, D, where it is completely dried. From D it passes through the train of weighed vessels, E, F, G and H, into a 15-litre bottle, I.

The vessels E and F contain the solution, and G and H the water and sulphuric acid respectively. The bottle, I, serves to damp down the changes of pressure caused by the air bubbling through the water in J. From J the air passes to the arrangement shown in fig. 8.

The process followed in an experiment was first of all to clean the vessels,

inside and outside, with a mixture of chromic and sulphuric acids, then after washing and drying the inside, the last branch of each vessel was filled with platinum tubes which had recently been ignited. The right quantity, about 28 c.c., of the various liquids was then measured into their respective vessels, and the latter, together with a closed counterpoise made of the same glass, and of the same shape and size as the vessels themselves, were washed and dried. It was necessary to pay great attention to the washing and drying, otherwise the amount of moisture which condenses on the vessel and counterpoise when on the balance pans will not be the same. They were, therefore, first washed with distilled water and then with pure alcohol, and finally dried with thoroughly dry fine linen dusters. The vessel and counterpoise were then weighed, against one another, by the method of double weighing,

FIG. 9.
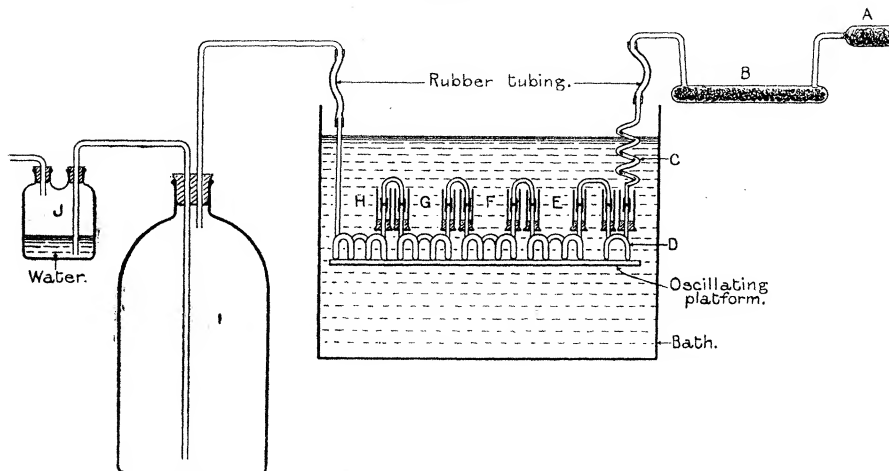
and the temperature of the balance case and the height of the barometer noted.

A special balance, made by Oertling, was purchased for this work, because ordinary balances are not fitted with pans large enough to take the vessels, and, further, the weight of some of the earlier forms of vessel was over 250 grammes. After weighing the vessels they were secured in their places on the platform and connected together by the joints already described; the whole was then lowered into the bath and the experiment started.

The rate of passage of the air was indicated by the rate of bubbling through J (see fig. 9), and it was kept, in the later experiments, as near as may be to 50 bubbles in 28 seconds. The length of time, during which an experiment lasted, varied with different concentrations. The order of

accuracy we aimed at was 5 per cent., and to reach this it was found necessary to obtain a loss of weight, in the vessel containing the water, such that the experimental error in weighing should not exceed 5 per cent. of the total loss. The experimental error in weighing one of the vessels was found to be under $\pm$ 0·0010 gramme, hence the loss of water should be at least 0·04 gramme.

The rate of bubbling mentioned gave this loss, with the weakest solution used (285 grammes of sugar in 1000 c.c.) in about 96 hours.

When the experiment was judged to be finished the vessels were taken out of the bath and washed, dried, and weighed as before—the balance temperature and height of barometer being noted for use in the reduction of the weights to a vacuum.

The table on p. 164 is a copy from the laboratory notebook of one of the later experiments. The solution used is 660 grammes sugar in 1000 c.c.

On taking down the vessels it was noticed that some water had condensed in the tube joining G and H, and its weight could not be satisfactorily estimated.

	Weight of vessel E.	Weight of vessel F.	Weight of vessel G.	Weight of vessel H.
Weight reduced to a vacuum—				
Before the experiment	23 ·0951	25 ·5783	4 ·2409	81 ·2665
After the experiment	21 ·5123	25 ·5770	4 ·1091	82 ·9759
Difference	1 ·5828	0 ·0012	0 ·1318	1 ·7094

Losses .... 1 ·7158
Gain .... 1 ·7094

Difference .... 0 ·0064
Mean corrected temperature .... 19°·47 C.

For the purpose of reducing the weights to a vacuum, the capacities of the different vessels and of the counterpoise had previously been determined, and, knowing the quantity of liquid put into the tubes, the data for the reduction is at hand.

In this experiment the vessel F, containing the second solution, lost 0·0012 gramme in weight. A similar loss was always experienced with cane-sugar solutions, but it will be remembered that with two vessels containing a sodium-chloride solution no appreciable loss was observed. The only difference that we could detect in the behaviour of these two solutions, when set up in an experiment, was that, on oscillating the vessel containing the cane sugar, there is a tendency for septa of the liquid to form

Date.	Time.	Bath temp.	Weight of vessel E.	Weight of vessel F.	Weight of vessel G.	Weight of vessel H.	Temp. of balance.	Barometer.	Time taken for 50 bubbles to pass.	Remarks.
October 27 ...	9. 45 A.M.		L 23·1894				10°·7	756·0		
	10. 5		R 23·1939	L 25·6676			10·8			
	10. 40		$\overline{23·1916}$	R 25·6719			10·9			
	11. 0			$\overline{25·6697}$						
	11. 35	19°·22			L 4·3352	L 81·3555	11·1			
	11. 55	19·22			R 4·3394	R 81·3606	11·4			
	12. 30 P.M.	19·22			$\overline{4·3373}$				secs.	
	12. 50	19·22							37	Started air current and oscillatory system.
	1. 10	19·23							31	
„ 28 ...	5. 5	19·23							28	
	9. 0 A.M.	19·24							28	
„ 29 ...	5. 15 P.M.								28	
	9. 0 A.M.								27	
„ 30 ...	5. 45 P.M.		L 21·6049				11·9	731·6	27	Took down.
	9. 0 A.M.		R 21·6094	L 25·6630	L 4·1993	L 83·0593	12·1			
	10. 30		$\overline{21·6071}$	R 25·6674	R 4·2037	R 83·0645	12·2			
	10. 50			$\overline{25·6652}$	$\overline{4·2020}$	$\overline{83·0619}$	12·3			
	11. 25									
	11. 45									
	12. 20 P.M.									
	12. 40									
	1. 15									
	1. 35									

across the tube just after the solution has run down to the lower end. These septa travel some distance with the air current before breaking.

With sodium chloride, however, the septa seldom form, consequently the loss of weight in the second vessel containing the sugar solution might be caused by the slight change of pressure resulting on the increase of work to be done by the air in moving the septa in the first vessel*—the loss is therefore quite analogous to that mentioned on p. 158.

The results of the experiments are given in the following tables :—

Experiments with Flat Spiral Tubes.

Date.	Concentration of cane sugar in grammes per 1000 c.c.	Temperature.	Hours run.	Rate of bubbling.	Loss in weight of solution.	Loss in weight of water.	Osmotic pressure.
1904.		°		secs.			atmos.
Nov. 12...	285	18 ·8	117	49	1 ·6219	0 ·0278	22 ·7*
„ 18...	285	18 ·6	109	41	1 ·8054	0 ·0380	27 ·8
Dec. 8...	285	18 ·3	117	46	1 ·5441	0 ·0315	26 ·9
„ 14...	420	18 ·2	69	43	0 ·9445	0 ·0317	44 ·0
„ 19...	420	18 ·3	86	40	1 ·2882	0 ·0394	40 ·2

* This experiment was carried out before the conditions necessary for accurate weighing were realised.

Experiments with Vessels described on p. 158.

Date.	Concentration of cane sugar in grammes per 1000 c.c.	Temperature.	Hours run.	Rate of bubbling.	Loss in weight of solution.	Loss in weight of water.	Osmotic pressure.
1905.		°		secs.			atmos.
June 11...	420	19 ·5	47	25	1 ·8624	0 ·0671	47 ·3
„ 14...	420	12 ·6	46	23	1 ·2136	0 ·0417	44 ·3
„ 19...	420	14 ·2	48	24	1 ·0984	0 ·0386	45 ·9
Aug. 8...	420	15 ·7	92	37	1 ·3935	0 ·0487	46 ·6
Oct. 6...	660	19 ·0	68	28	1 ·5896	0 ·1309	105 ·7
„ 13...	660	19 ·4	68	28	1 ·6515	0 ·1324	103 ·2
„ 27...	660	19 ·5	68	28	1 ·5822	0 ·1318	107 ·0

It will be noticed that in the experiments with the spiral tubes the loss of the water is less than 0·04 gramme. These experiments were made before we had been able to appreciate the experimental errors.

* Mr. Whetham suggested this explanation to us.

The numbers under the column headed "Osmotic pressure" are calculated from the equation $P = \dfrac{As}{\sigma} \log_e \dfrac{p}{p_1}$, where P is the osmotic pressure, p the vapour pressure of the water, p_1 the vapour pressure of the solution and s the density of water at the temperature of the experiment, σ is the vapour density of water vapour under the standard atmosphere, A. The discussion of this equation is given below.

Theory.—When the results of our vapour-pressure experiments were used for calculating the osmotic pressures by means of Arrhenius' well-known relation :—

$$P = \frac{A\rho}{\sigma} \log_e \frac{p}{p_1} \qquad (1)$$

(this equation differs from the one given above only in that the density of the solution ρ replaces s, the density of the solvent), it was found that they differed considerably from those measured directly.

For instance, the two values of the osmotic pressure of a solution of cane sugar in water—

Of 285 grammes to the litre differed by about 5 per cent.
„ 420 „ „ „ „ 15 „
„ 660 „ „ „ „ 30 „

It was thought, at first, that these discrepancies were due to some error in the vapour pressure method, and numerous experiments, previous to those given in the second table, but not tabulated, were carried out to throw light on the subject.

Eventually Equation (1) was examined more closely. As this examination led to a result which does not seem to be generally known, we take the opportunity of drawing attention to the subject. This we do the more readily, in that Mr. Spens has come independently to a similar conclusion[*] by starting from a different point of view.

It is necessary to recapitulate briefly part of the reasoning by which Equation (1) is derived. In fig. 10, AB is a vessel closed at the lower end by a semi-permeable membrane, B, and filled with a solution to a height BA above the solvent, C, such that the vapour pressures of the solvent and solution are in equilibrium at A.

If ρ be the density of the solution and p_1 its vapour pressure, p the vapour pressure of the solvent at C, and P the osmotic pressure; then, by considering the pressures about the membrane, it is easy to see that

$$P + p = gh\rho + p_1 \text{ (where } h = BA).$$

* See paper published *infra*.

But $p - p_1$ is very small compared to the osmotic pressure of a strong solution, and can therefore be neglected; then

$$P = ghs. \tag{2}$$

It is evident that this relation is true only when the density and concentration are the same throughout the column AB. A 30-per-cent. solution of
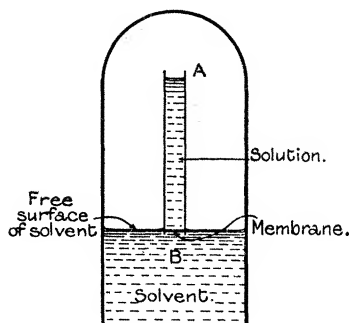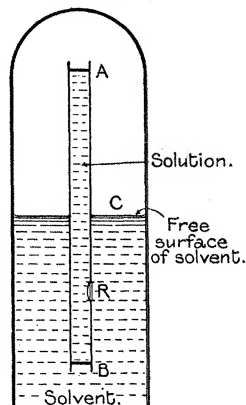

FIG. 10.

FIG. 11.

sugar in water would be in equilibrium when standing in a column some 500 yards high. In a long column such as this, there is no reason for supposing that the density and concentration are constant throughout. In fact, it is easy to show that a difference in concentration, and therefore a difference in density, must take place.

Thus in fig. 11 let the lettering have the same signification as in fig. 10; the only difference in the two figures is that the tube is prolonged downwards and the membrane B is below the surface of the solvent.

If we assume that the density of the solution is higher than that of the solvent, then the hydrostatic pressure on B is in this case greater than in fig. 10, by an amount $g\mathrm{BC} \times \rho - g\mathrm{BC} \times s$, where ρ and s are the densities of the solution and solvent respectively. It follows that the osmotic pressure at B, in fig. 11, is greater than that at B in fig. 10, and the only cause which can produce this is a difference of concentration at the two points.

Van Calcar and De Bruyn* have shown that solutions can be concentrated by centrifugalisation; the force of gravity acting on the solute molecules would of course produce a similar effect.

Be this as it may, if we regard it as proved that the density and concentration of the solution at the top and at the bottom of the column are

* 'Rec. Trav. Chem. Leiden,' vol. 23, pp. 218—223, 1903.

not the same, then Equation (2) will only be true if we substitute for ρ, the averaged density between the limits ρ_A and ρ_B, where ρ_A and ρ_B are the densities at the top and bottom of the column. P will then be the osmotic pressure at the bottom of the column in fig. 10.

A direct measurement of osmotic pressure evidently gives the osmotic pressure corresponding to the concentration at the top of the column, it is therefore necessary to obtain an equation connecting this with the same pressure derived by way of the vapour pressures.

The following investigation gives the required relation :—

Consider fig. 11.—If another semipermeable membrane be opened at R, the equilibrium will not be disturbed, otherwise perpetual motion would result.

If P_R denote the osmotic pressure at R, and h the height above B, then, from a consideration of the hydrostatic equilibrium of the column BR,

$$P_R + \text{pressure of column BR of solution} = P_B + \text{press. col. BR of solvent,}$$

$$\therefore P_R + \int_B^R g\rho\,dh = P_B + \int_B^R gs\,dh,$$

$$\therefore P_R = P_B - \int_B^R g\,(\rho - s)\,dh. \tag{i}$$

But the hydrostatic equilibrium up to A gives

$$P_B = \int_B^A g\rho\,dh - \int_B^C gs\,dh - \text{pressure of column AC of vapour.} \tag{ii}$$

By a process similar to (i)

$$P_A = P_B - \int_B^A g\,(\rho - s)\,dh.$$

Substituting in (ii)

$$P_A = \int_B^A g\rho\,dh - \int_B^C gs\,dh - \text{vapour AC} - \int_B^A g\rho\,dh + \int_B^A gs\,dh$$

$$= \int_C^A gs\,dh - \text{pressure of column CA of vapour.} \tag{iii}$$

It will have been noticed that our experimental results differ from one another by about 5 per cent. The pressure of the column CA of vapour is evidently negligible compared with the osmotic pressures we are measuring ; and, as compared with the experimental errors, the compressibility of the solvent, water, and the change in the force of gravity due to height above sea level, are also negligible.

Equation (iii) may therefore be replaced by $P_A = gs\text{CA}$.

The only change in Equation (2), and therefore in Equation (1), necessary to give the osmotic pressure at the top of the column is the substitu-

tion of the density of the solvent in place of the density of the solution. On making this correction it was found that the osmotic pressures derived from our vapour-pressure measurements and those observed directly, agreed to within 5 per cent.

This communication should be regarded partly in the light of a preliminary paper. It is published now, because we think the limited number of experiments are sufficient to establish the primary object we had in view, namely, to prove the method we have adopted for the direct determination of osmotic pressures. We learn from a reference in 'Science'* that Professor Kahlenberg recently read a paper before the American Chemical Society describing what appears to be a dynamic method similar to ours.

The various precautions taken have been described at some length, because we think that successful results can only be obtained by paying great attention to the details of the experiments. We are glad to have this opportunity of thanking Mr. Whetham for the kindly interest he has taken in the work.

* "On a New Dynamic Method of Measuring Vapour Tensions of Solutions," 'Science,' July 21, 1905.